

Ligand Influence on Metal Aggregation: a Unique Bonding Mode for Pyridylpyrrolides

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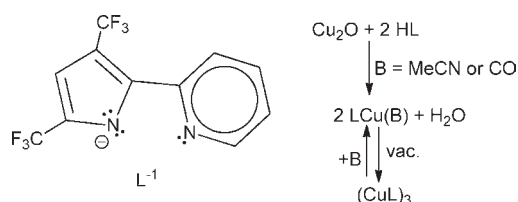
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The synthesis and characterization of a Cu^{I} complex with a cis-bidentate monoanionic nitrogenous ligand, 2-pyridylpyrrolide, L, is reported. This shows binding of one base B = MeCN or CO per copper in a species $\text{LCu}(\text{B})$, but this readily releases the volatile ligand under vacuum with aggregation of transient LCu to a mixture of two enantiomers of a chiral trimer: a zwitterion containing inequivalent Cu^{I} centers, possible via a new bonding mode of pyridylpyrrolide, and one with nitrogen lone pairs donating to two different metals. Density functional theory calculations show the energetics of both ligand binding and aggregation (including dimer and monomer alternatives), as well as the ability of this ligand to rotate away from planarity to accommodate a bridging structural role. The trimer serves as a synthon for the simple fragment LCu .

The coordination chemistry of monovalent copper offers some characteristics that allow unusual function.¹ It is very versatile in adopting coordination numbers 2–4, with the first of these having only 14 valence electrons. Finally, the large number of nuclear protons leaves the monovalent copper a very poor π base, showing little evidence (by its ligand selectivity and by the lack of reduction of the CO stretching frequency in its carbonyl complexes) for π -back-bonding to such ligands.² This means that CO is reversibly bound (reversibility being an unusual feature of this typically “strong” ligand), and thus even CO can serve as a good leaving group; for example, scavenging and later release of CO impurity is possible.

Bidentate ligands bearing one anionic donor atom that can serve a bridging (μ_2) role, RO, RS, R_2N , and even phenyl, are suitable for avoiding bent two-coordinate monomers by aggregation into $[\text{Cu}(\mu_2\text{-X})]_n$ oligomers. Special situations arise when the anionic ligands on Cu^{I} lack such a bridging ability and have convergent lone pairs, which makes mono-

Scheme 1



meric two-coordinate complexes unfavorable because of their constrained nonlinear geometry.³ Disproportionation of copper is then one decomposition mode. Thus, while 2-pyridylpyrrolide ligands (L^{-1} ; Scheme 1) have been shown to form many bidentate monometallic complexes,^{4–10} its convergent donor sites make it not so obviously suited for bridging two metals.

We report here studies of such a convergent bidentate, monoanionic ligand on Cu^{I} , as well as factors that influence the extent to which aggregation can play a role in the equilibria available to such a system. This includes results with this pyridylpyrrolide ligand that show both lability and ready (i.e., fast) reorganization of Cu^{I} to accommodate a scarcity of ligands. What also becomes evident is a unique structural capability of pyridylpyrrolides.

This ligand L^{-1} can be installed¹¹ on monovalent copper by the reaction (Scheme 1) of Cu_2O with HL in acetonitrile. The reaction is complete within less than 1 h at 25 °C and is signaled, monitoring NMR spectra during the reaction, by a change of all proton and ¹⁹F NMR signals of free HL to those of the product, together with a loss of the pyrrole NH proton and growth of the signal at 2.15 ppm due to liberated water. All-protio crystalline $\text{LCu}(\text{NCMe})$ can be isolated by slow

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concentration and then cooling and shows a ^1H NMR signal integrating for one MeCN ligand. In the presence of variable amounts of added free MeCN, only one coalesced ^1H NMR signal is seen for free and coordinated MeCN, indicating rapid exchange on the NMR time scale. Monovalent copper chemistry with these pyridylpyrrolide ligands L^- is generally complicated by essentially immediate equilibrium shifts when a new Lewis base is added or when a volatile Lewis base is lost under the vacuum removal of a solvent. These changes are sometimes best recognized by a change of color and less often by a change of NMR spectra, with the latter often suffering line broadening due to intermediate regime dynamic broadening.

It is possible to do the synthesis with HL even in nonpolar benzene if a monodentate donor is provided to “stabilize” the otherwise two-coordinate product. Thus, HL reacts with Cu_2O within 6 h at 25°C under 1 equiv of CO to give $\text{LCu}(\text{CO})$. The key parameter of this molecule is its CO stretching frequency, 2106 cm^{-1} , showing the presence of only one CO ligand, with very little π -back-donation. The calculated [density functional theory (DFT) B3LYP/cc-pVTZ(f)] reaction energy for competition between CO and MeCN for the LCu fragment favors coordinated CO by 3.6 kcal/mol. We interpret this small difference for such electronically different ligands as showing no great preference for the clearly more powerful π acid, CO, hence also evidence for the unimportance of π -back-bonding in these adducts; in practice, equimolar MeCN completely displaces volatile CO from $\text{LCu}(\text{CO})$ in time upon mixing in benzene. The reaction energies for binding CO (and MeCN) to bent monomeric LCu (vide infra), are -35.3 (-31.6) kcal/mol. The reaction energies for binding of a second CO (or MeCN) to LCu (monodentate) are -6.5 (-4.0) kcal/mol, respectively. This weak binding energy to form four-coordinate copper shows that three-coordinate species $\text{LCu}(\text{B})$ are not Lewis acidic.

The binding of CO is shown to be completely reversed (without any evident change from colorless) simply by exposure to a vacuum at 25°C , and recoordination of CO was proven by subsequent exposure of the CO-free material to CO in a benzene solution. The same reversibility is true for the MeCN adduct. This resulting very air-sensitive, diamagnetic MeCN- and CO-free material in benzene shows six different ^{19}F NMR chemical shifts, consistent with (at a minimum) three chelates per molecule, and shows a number of ^1H NMR chemical shifts to confirm that same conclusion; the molecule is thus at least a trimer. This conclusion also requires the (unusual for Cu^{I}) assumption that the structure is not fluxional on the ^1H and ^{19}F NMR time scales; even at $+60^\circ\text{C}$, there is no coalescence of the ^{19}F NMR signals, and no evidence of fragmentation into different oligomers. Thus, the fragment CuL avoids a two-coordinate bent structure by aggregation, yet that aggregation is reversed upon the addition of CO or MeCN. The mass spectrum of “ LCu ” shows only the ion $\text{Cu}(\text{L})_2^+$, which we attribute to the aggregated nature of “[CuL] $_n$ ”, and thus the ability of two chelates to cluster around a single copper under ionization conditions (bimolecular collisions and collisions between like-charged species are unlikely at the pressure of the mass spectrometer).

We evaluated (DFT) the energetics of monomer versus dimer versus trimer CuL . We found stationary states for all three structures, but their electronic energies show both the dimer and trimer to be decisively favored versus the monomer, both because of the poor suitability of a bent two-coordinate structure for the monomer. For this same reason,

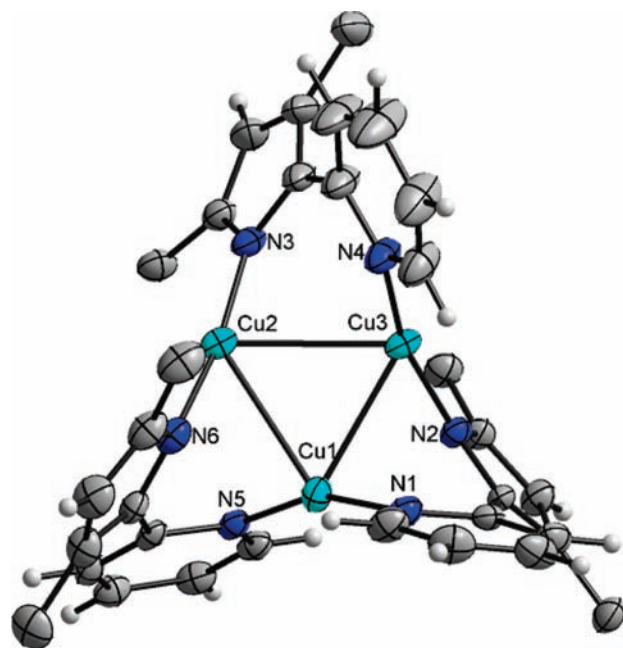
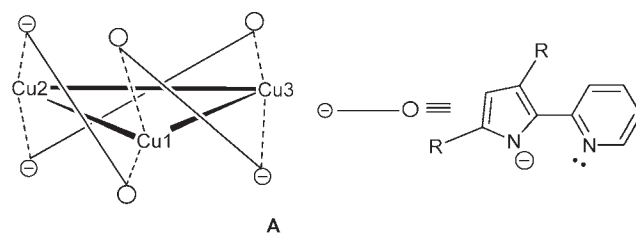


Figure 1. ORTEP view of the non-hydrogen atoms of $(\text{LCu})_3$, showing 50% atom probabilities. Unlabeled atoms are carbon atoms; fluorine atoms on the CF_3 groups are omitted for simplicity. Selected structural parameters: Cu1-N5 , 1.9098(19) Å; Cu1-N1 , 1.9147(19); Cu2-N3 , 1.881(2); Cu2-N6 , 1.887(2); Cu3-N2 , 1.8809(18); Cu3-N4 , 1.890(2); Cu1-Cu3 , 2.6875(4); Cu1-Cu2 , 2.7924(4); Cu2-Cu3 , 2.8572(4); N5-Cu1-N1 , 157.51(8); N3-Cu2-N6 , 171.35(8); N2-Cu3-N4 , 162.41(9); Cu1-Cu2-Cu3 , 56.795(10); Cu1-Cu3-Cu2 , 60.388(10); Cu3-Cu1-Cu2 , 62.817(11).

it is very favorable (-20.5 kcal/mol) for the monomer to add to a dimer to make a trimer.

A DFT survey¹² of numerous helical trimer geometries revealed one (A) which accomplished C_3 -symmetry breaking by the reversal of one chelate from the C_3 arrangement (drawing A, which shows the helical character). While this was the most stable structure, other C_1 species were also found to be only ~ 6 kcal/mol higher;¹¹ this trimer thus has numerous energetically competitive structural minima. Structure A has each pyridylpyrrolide linking two metals, made possible by strong twisting of the chelate away from planarity, in contrast to its usual role⁴⁻¹⁰ as a cis-bidentate ligand attached to a single metal. This twist disrupts any inter-ring conjugation (penalty ~ 4 kcal/mol $\cdot \text{L}$ by DFT) and thus increases the nucleophilicity of the pyrrolides. The structure has two pyrrolides attached to one copper (Cu2) and, hence, two pyridyls attached to another copper (Cu1); it is apparently the zwitterionic character that is energetically favorable, and this is what causes the reduction from a C_3 -symmetric structure.



The structure of crystals grown from benzene (Figure 1) confirms the absence of any symmetry (but a racemic mixture

(12) For C_3 -symmetric Cu^{I} trimers, see: (a) Singh, K.; Long, J. R.; Stavropoulos, P. *Inorg. Chem.* **1998**, *37*, 1073. (b) Singh, K.; Long, J. R.; Stavropoulos, P. *J. Am. Chem. Soc.* **1997**, *119*, 2942.

in the crystal) because of the fact that only one copper bonds to one pyrrolide and one pyridyl; another copper binds two pyrrolides, and the last copper binds two pyridyls. The molecule is thus a zwitterion with one $\text{Cu}(\text{pyridyl})_2^+$ and one $\text{Cu}(\text{pyrrolide})_2^-$ in the triangle. Each copper is approximately linearly coordinated by two nitrogen atoms, as well as whatever interaction comes from two neighboring copper centers. Every pyridylpyrrolide ligand binds to two metals, and dihedral N–C–C–N angles are in the range 36.8–47.4°, hence, halfway between staggered and eclipsed; the ligand is thus highly suited for bridging. The six Cu–N distances vary over only 0.03 Å. It is worth noting that the copper with two pyridyls, i.e., the cationic center Cu1, has two additional short contacts, 2.590 (N6) and 2.619 (N2) Å to pyrrolide nitrogen atoms. This $\text{Cu}(\text{pyridyl})_2^+$ unit is what is extracted in the mass spectroscopic process, and its integrity is reinforced by the two pyrrolide interactions with this electron-deficient copper. Bridging pyrrolide has been detected previously,¹³ although it is not at all common; it speaks for high nucleophilicity at the pyrrolide nitrogen atom and thus ability to break what aromaticity the pyrrole 6 π -electron system possesses, via nitrogen bridging and nonplanarity of the pyridylpyrrolide. There are no Cu/F interactions (distances > 2.84 Å).

In summary, what happens when a convergent monoanionic bidentate ligand/ M^I combination is depleted of a third

ligand? How can the resulting monomer avoid the undesirable *bent* two-coordinate structure? The answers provided here for pyridylpyrrolides reveal ligand-driven phenomena. This work demonstrates the ready reorganization of these CuL species in innocent solvents, in spite of the chelate effect that might have been expected to slow aggregation equilibria. The mass spectral data support the retention of aggregates in the vapor phase (being the source of CuL_2^+ fragments, the formula of which indicates an unusual redox character from Cu ($\text{Cu}^{3+}\text{L}^-\text{L}^-$) or L ($\text{Cu}^{2+}\text{L}^0\text{L}^-$ or $\text{Cu}^+\text{L}^0\text{L}^0$)), and the ready disruption of the trimer upon the addition of MeCN or CO proves the latent reactivity of the trimer, which thus serves as an effective synthon for monomeric CuL. The pyridylpyrrolide bridging is a capacity rarely observed¹¹ for the otherwise analogous bipyridyl ligand. Both the thermodynamics and aggregation phenomena exhibited here show that bent monomeric two-coordinate Cu^I is an unattractive and, hence, highly reactive species.

Because the trimer is a source of three Cu^I moieties and is strongly air-sensitive, we are currently exploring its atom-transfer reactivity. The possibility of regulating the aggregation by changing the pyrrolide substituents is also being addressed.

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Supporting Information Available: Full experimental and computational details, including CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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